# This Page Is Inserted by IFW Operations and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

### IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

F Schambil and M. Böcker, Dusseldorf/Germany

## Detergent Tabs - One Year after their Pan-European Launch\*

In recent years, tablets have gained a big share of the European market in various product categories such as automatic dishwashing detergents and bleach boosters. The pun-European launch of detergent tabs from late 1997 marked the creation of a new segment It is not yet possible to predict the future size in the tablet segment in the heavy duty detergent market.

In den letzten Jahren haben Reinigungsmittel in Tablettenform einen großen Anteil am europäischen Markt bei Produktarten wie Maschinengeschierspulmittel und Bleichboostern gewonnen. Mit der europaweiten Einfuhrung von Wuschmittel-Tabletten ab Ende 1997 ist ein neues Marktsegment geschaffen worden. Zur Zeit läßt sich der zukünftige Marktanteil der Tabletten bei den Universalwaschmitteln noch nicht abschatzen.

#### 1 Introduction

The detergents and household cleansers market in Europe has been shaped by a series of major innovations during the last 10 years. This report deals with the current status of developments in the field of detergents and household cleansers in tablet form. The focus is on the detergent tabs that were first introduced in Europe in late 1997

Tablets were first launched on the household cleansers sector in Europe in the early 1990s. Within a short time they were followed by laundry additives such as water softeners and bleach boosters. Toilet cleaner tabs were also introduced. In Germany, tabs now account for about 60% of the automatic dishwasher detergent market. Finally, from late 1997, detergents in tablet form were introduced in a large number of European countries.

	ADD tabs	HDD tabs
Disintegration	15 min	30 sec – 5 min
Temperature	50 - 65 °C	cold water
Amount of "free water"	n <sub>i</sub> gh	iOw
Specific ingrealents	-	surfactants

Fig I Requirements on tubs

Market research indicates that consumers find tabs more convenient than powder detergents and appreciate their greater efficiency. Tabs are easier to dispense, the dosage table is easier to understand, and no dosing and dispensing aids are needed. Other advantages include the avoidance of over and under dosage, both of which result in consumer dissatisfaction with the product, and the smaller package format of the product in this highly concentrated form. The elimination of dosing aids is of considerable ecological benefit, as is the tablets ability to dispense exact amounts. The environmental compatibility of heavy duty detergent tabs was recently confirmed by the German environmental organization "Deutsche Umwelthilfe" (Radolfzell, Germany).

#### 2 Demands made on detergents and household cleansers in tablet form

Tabs in the detergents and household cleansers sector have widely different requirement profiles. A comparison of automatic dishwashing detergent (ADD) tabs and heavy duty laundry detergent (HDD) tabs is especially interesting (Fig. 1). ADD tabs should not dissolve until the prewash cycle has finished and the main wash has started, but HDD tabs do have to disintegrate within seconds, and certainly within only a few minutes, depending on how they are dispensed, because short washing programs only last about 20 minutes. The water temperature in an automatic dishwasher during the main wash is between 50° and 65°C. In contrast, the water that runs into a washing machine at the start of the wash cycle is still cold. The amount of "free" water in a dishwasher during the main wash is relatively high, whereas a high proportion of the water in modern washing machines with an automatic volume control system is absorbed by the wash load. The requirement for HDD tabs to disintegrate rapidly is especially challenging. The amonic and nonionic surfactants contained in heavy duty detergents may form viscous liquid crystalline phases ("gels") when they come into contact with water, and these gels may hamper a quick disintegration of tabs

#### 3 Disintegrants

As a rule, tablets should disintegrate rapidly in water. One exception to this rule is ADD tabs, which are not introduced via a dispensing compartment but are placed directly in the dishwasher before the prewash cycle. Tablets that disintegrate rapidly, such as water softener, bleach booster and laundry detergent tabs, usually contain disintegrants. These aids, some of which are also used in the pharmaceuticals sector, can be classified into four groups:

<sup>\*</sup>Lecture given at the 13th Meeting of the GDCh-Special Group Waschmittelcheinie" Wurtzburg, Gennany, May 3-4, 1999

- effervescent systems, such as a combination of hydrogen bicarbonate and curic acid, which generate gases when they come into contact with moisture
- swelling agents, such as cross-linked polyvinyl pyrrolidone (PVP) or carboxymethylcellulose, whose volume increases considerably when they are exposed to moisture, leading to a buildup of internal pressure
- fast dissolving substances such as acctate or citrate, which are thought to increase the capillarity of tabs, thus promoting rapid water transport into the tablet.
- water-soluble coatings, with a loose structure inside the rab (Fig. 2).

In practice, combinations of different disintegrants are frequently employed

Besides the type and amount of disintegrant, the formulation and the properties of the granulate used for tableting have a considerable influence on disintegration.

Other tableting aids that are used in the pharmaceutical industry, such as binders and lubricants, are present in only very small amounts in some tabs.

#### 4 Characterization of tabs

26-11-03

One of the main factors influencing the application-related properties of tabs is their composition. Another important factor is the compression force applied during tableting. The maximum tolerable compressing force depends on characteristic properties of the starting products such as density, particle size distribution and water content.

A vanety of methods are suitable for characterizing tabs. Their hardness is usually determined as diametral fracture stress. Speed- and force-controlled semiautomatic measuring instruments exist for this purpose. They measure the force that has to be applied before the tab breaks. The friability of the tablets can be measured with a rotating glass vessel. The amount of abrasion of the tab after a given time under a given load is measured. Disintegration can best be determined visually, e.g. by placing a tab on a suitable support in a beaker with water. The pharmaceuticals sector makes use of disintegration testers that subject tablets to up-and-down motion in a plastic holder with holes in its base.

As a rule, tableting produces very compact products. The example of heavy duty detergents illustrates that the transition from traditional powders (spray products) via compact products (extrudates/granulates) to tabs is associated with a clear increase in density (Fig. 3). This yields benefits in terms of package volumes, transport and the necessary storage space and outlet shelf space.

- 1. Effervescents
  NanCO<sub>3</sub> / citric acid
- 2. Swelling agents
  PVP crosslinked, cellulose, CMC
- 3. Highly water-soluble substances Na (K) acetate, Na (K) citrate
- 4. Water-soluble coating Dicarboxylic acid

Fig 2. Distinegrants for tubs



Fig 3. Density of HDD tabs

#### 5 Composition and properties of detergent tabs

Detergents in the form of tablets were launched in the USA as long ago as the early 1960s. They were not very successful, possibly because of their unsatisfactory disintegration and solubility properties, and they soon disappeared from the market. Since the mid 1980s a bleach-containing laundry detergent tablet has been available in Spain, which has maintained a low but stable market share.

Specific demands are made on detergent tabs. They must be hard enough to withstand being packaged, transported to the warehouse and the customer and then used in the home. Fast disintegration and good solubility, even in cold water, are essential to good washing power and the avoidance of residues in the washing machine or on textiles.

In view of the high surfactant content of modern HDD, the development of fast disintegrating detergent tabs poses special challenges (Fig. 4). In certain temperature and concentration ranges, surfactants form lyotropic liquid crystalline phases with a high viscosity. In detergent tabs these liquid crystals can delay disintegration by, for example, inactivating the disintegrant. Highly viscous liquid crystalline phases also prevent more water from penetrating into the tab. Antigelling agents, distinct surfactant combinations and highly effective disintegrants – i c, types that swell within seconds – are used to prevent these

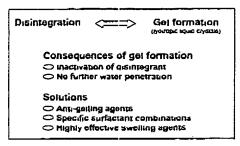


Fig. 4 Disintegration of surfactant based tabs

undesirable effects from occurring. Another possibility is to press the detergent raw materials only lightly and then, after the tableting process, to provide the tabs with a coating.

Companson of the key physical parameters of the HDD tabs currently available on the market reveals certain similarities and differences (Fig. 5). The diameter of the tabs (between 40 and 45 mm) is clearly greater than that of ADD tabs. The weight of the HDD tabs depends on the recommended dosage and is between 36 and 43 g. All

#### F. Schambil and M. Bocker Detergent Tabs - One Year after their Pan-European Launch

From-PATENT DEPARTMENT PORT SUNLIGHT

Diameter	40 – 45 mm	
Veignt	36 – 43 g	
Fracture Stress	40 - 80 N	
Number of layers	1 or 2	
Packaging	single or double flow-pack	

Fig. 5 HDD lubs

producers recommend using 2 tabs for medium soiled laundry and medium water hardness. HDD tabs have to disintegrate quickly, so their hardness or breaking strength is much lower than that of ADD tabs. One-phase and twophase HDD tabs are commercially available. Two-phase tabs contain components that could react with each other during storage and are therefore kept apart in the two phases.

All HDD tabs are packed either singly or in pairs in flowpacks. Individually packed tabs exhibit several advantages: better protection against moisture, better chemical stability, better retenuon of fragrance, avoidance of direct skin contact during dosage and mechanical protection during transport

The HDD tabs that are available on the market are dispensed in a variety of ways. Interestingly, each of the four Big Soapers recommends a different dispensing option. Placing the tabs into the drum without the help of a dispensing and poses problems. In modern water-saving washing machines such as those that have been available in northern European countries since the mid 1980s and in southern Europe since the early 1990s, the water level during the usual wash cycle is very low. At the start of the reverse cycle, tabs dispensed into the empty drum may come to rest on the rubber gasket of the door of the washing machine Because the water level is lower than the rubber gasket, disintegration may be delayed, so that the tabs subsequently do not dissolve fast enough. The washing result will be less satisfactory than it should be. Foam may form during rinsing cycles, bringing with it a risk of residues on the textiles at the end of the wash cycle.

As an alternative, tabs can be used via dispenser. The tabs will, however, have to disintegrate in a very short time with very little water. This option has a number of advantages,

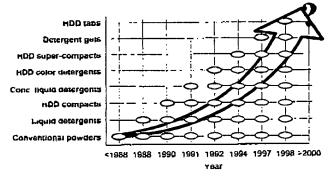


Fig 7 Heavy duty detergents in Western Europe

50

such as convenience, fast disintegration so that the tab's detergency takes immediate effect, avoidance of so-called pin hole spotting (local irreversible discoloration of colored items when textiles come into contact with bleachcontaining detergents) and avoidance of residues on textiles

Zeolite or phosphate based HDD tabs are now available (Fig. 6). In terms of their composition, HDD tabs differ from other compact detergents only in respect of the disintegrants. However, all compact heavy duty detergents in Europe have been zcolite-based until now. The reappearance of phosphate in this product category is, therefore, a remarkable development.

	Zooina Dased	Рпозр <u>пат</u> пасод %
SURTECTARDE (FAS. LAS. FAEO, APG)	13 - 18	15-18
Bloaching agents	13 - 16	12 - 16
TAED	3-7	4-7
Zeolite (A P)	11 - 25	1 -
Phosphate	-	25 - 47
Lavered SINCETO	D-9	-
Coporymer	2-3	2
Diormogrami	5-17	0-12
Enzymes	2 – 4 artt	2 - 3 att

Fig 6. Composition of HDD tabs

#### 6 Market situation of detergent tabs in Europe

The launch of HDD tabs by major detergent producers in Europe started in late 1997. One of these producers already has a pan-European presence, while another is represented in a large number of countries. The market shares in the individual countries still differ significantly due to the different weighting of compact products and traditional powders and the different launch times. In some countries, private label tabs have also already been introduced.

A review of the development of heavy duty detergents in the last ten years in Europe (Fig. 7) shows that until 1987 only classic spray-dried products were available. Within just a few years this type of product was in some European countries almost completely driven from the market by compacts and, shortly afterwards, supercompacts Liquid detergents, which were joined by liquid concentrates and gels a few years after their introduction, have also sold very successfully in some European countries. The next few years will show whether detergent tabs can also become an important segment.

#### The authors of this paper

Or Monika Bocker, born in 1959, studied Organic Chemistry at the University of Münster. After her PhD in 1986, she worked as a post-doc in the field of carbohydrate chemistry. In 1987, she joined Henkel KG3A in Dusseldorf to work in the Applied Research/Product Development Detergents and Cleansers.

Dr. Fred Schambil, born in 1951, studied Physical Chemistry at the University of Cologne After his studies, he was post-doc at the Max-Planck-Institut (Dusseldorf) In 1981, he joined Henkel KGaA in Dusseldorf to work in the Physical Chemistry department Early 1990 he relocated to Henkel Research Corporation (Santa Rosa, USA). Since mid 1991, he has been working on detergents, currently as Director Applied Research/Product Development Detergents